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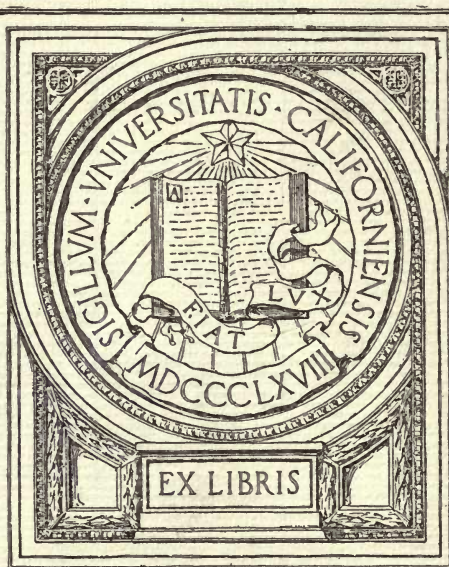
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# Studies in Adsorption

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## A THESIS

SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL  
OF THE UNIVERSITY OF MINNESOTA  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

BY

EARL PETTIJOHN

June, 1918







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# Studies in Absorption

## A THREE

THE UNIVERSITY OF CHICAGO  
DEPARTMENT OF CHEMISTRY  
IN PRESENTATION OF THE RESULTS OF  
RESEARCHES ON  
THE ABSORPTION OF  
LIGHT BY  
SOLIDS

UNIVERSITY OF CHICAGO  
PRESS

CHICAGO, ILL. 1914

# Studies in Adsorption

## PART I.—AN ATTEMPT TO DETERMINE APPROXIMATE GRAIN SIZE AND THE MEASUREMENT OF THE MAXIMUM THICKNESS OF SURFACE FILMS.

**Introduction.**—The determination of mean grain size is of importance in a number of problems. Among these are problems involving the flow of water through soil and adsorption problems. In the first case grain size determines the number, size and kind of pores through which the water flows, in the second it determines the amount of surface available for adsorption. In the former case King<sup>1</sup> has done some work on estimating pore space and relating the rate of flow to the diameter of the grain; in the latter, mass is universally substituted for surface, a procedure which is apt to introduce a variable error. The first part of this paper deals with a new method of estimating the diameter of small grains and gives results for materials of known surface.

The thickness of water films formed on glass and sand has been investigated quite fully. The second part of the paper describes a simple method of determining the maximum film which can form on materials of this kind.

### Materials.

**Sand.**—Ordinary river sand was used. It was treated with concentrated hydrochloric acid until no test for iron was shown. The acid was then washed out with distilled water and the sample dried in the air. Four samples were obtained by sifting. The first sample contained all of the sand which passed the ten-mesh screen but was retained by the twenty-mesh screen. The second, third and fourth samples consisted of the fractions from the original lot retained by the forty-, sixty- and eighty-mesh screens, respectively. These are called ten, twenty-, forty- and sixty-mesh sands in this paper.

The grains in this lot of sand were far from spherical, no two diameters being the same. An approximation of the surface was obtained by weighing a counted number of grains (4000 to 5000), to get the average weight per grain, and determining the specific gravity. On the assumption that the grains were spherical the diameter and surface of a single grain could be calculated. It was realized when these values were obtained that they were at best only approximations.

**Ottawa Sand.**—A single sample of sand called in this paper "Ottawa Sand" consisted of well rounded grains. This sample gave values by the above mentioned method which were very close to the true value for the diameter and surface. It was considered to be of known surface.

<sup>1</sup> Nineteenth Annual Report Geological Survey, 1897-98, pages 67-294.



**Glass Pearls.**—The glass pearls used were solid, round and of various sizes, as indicated in the table below. A few, which were poorly formed were removed from the lot by rolling them down an inclined board. Those which were not round could be easily picked out in this way. The pearls were from two different sources, and apparently of different kinds of glass. They differed considerably in specific gravity.

The first lot was purchased retail. The material was sold under the name of "glistening dew" and was used to decorate fancy cards. Two samples were obtained from this lot by "elutriation." A quantity of the pearls were placed in a tube and delivered from it at a slow rate into a rising column of water. Under these conditions by properly regulating the current, the lighter ones were carried up and the heavier ones sank to the bottom. These samples are No. 9 and No. 10, in the tables.

The second lot consisted of five samples, Nos. 1, 3, 5, 7 and 8. The individual pearls in each sample were of the same diameter except for No. 7 which contained pearls of two sizes. These samples were obtained from Germany and when received were coated with dye.

All of the samples were cleaned by boiling in concentrated nitric acid, washing free from acid and air drying. The diameter surface and volume of the pearls in each lot was determined by the method used for the sand. Since the pearls were very nearly spherical in form they were considered to be of known surface.

**Precipitated Silica.**—Precipitated silica was only used in the preliminary work in this paper. No attempt was made to determine the surface or diameter of the particles of the powder accurately. The microscope showed it to be very fine, but far from uniform. The sample used was of German origin. It was necessary to wash free from iron before using it.

The following table gives the weights and the specific gravities of the materials used.

TABLE I.  
Data on Materials Used.

Samples. Sand.	Mean weight of single grain in gram.	Specific gravity.
10-mesh	0.000168	2.643
20-mesh	0.000110	2.645
40-mesh	0.000030	2.650
60-mesh	0.000007	2.666
Ottawa	0.000686	2.656
Pearls	....	....
No. 1	0.003988	3.101
No. 3	0.002625	3.090
No. 5	0.000853	3.079
No. 7	0.000261	3.125
No. 8	0.000121	3.069
No. 9	0.000182	2.505
No. 10	0.000122	2.496



## Part I.—General Considerations.

There are at present three methods of determining the surface of small grains. They are:

1. Count-weight Method.
2. Average Diameter Method.
3. King's Method.

The count-weight method has already been described, it being the method used in the calculation of the diameter and the surface of the samples used in this piece of work. It is accurate only if the particles are spherical and of the same diameter.

The average diameter method consists in measuring the diameter of a large number of grains and using the average obtained for calculating the surface and volume. It will also give accurate results if the grains are spherical and of very nearly the same diameter. This method as well as the former one may give results far from the actual ones for grains that are not spherical.

King's method consists in determining the time taken for a given volume of air or water to pass through a certain packed volume of the material to be tested. A formula,

$$Q = \frac{psd^2}{h\pi k} \quad (1.1846)$$

is given for the amount of air flowing through the apparatus in a given time. The quantity for unit time varies with the square of the diameter. The method is a first attempt to determine diameter and surface independent of the individual particle. The above equation is derived from a mathematical study of the factors involved in the passage of air through such a medium. The equation and the experimental results reported by King check with a fair degree of accuracy.

The method described in this paper is in some respects similar to that of King, the results being derived from the rate at which water is removed from the surface instead of the rate at which air passes through a mass of packed grains.

**Experimental Work.**—The first work done was of a preliminary nature and was carried out for the purpose of determining the magnitude of the changes that could be expected with the materials used.

Air dry samples of Ottawa sand, ignited and unignited silica, and twenty-, forty- and sixty-mesh sands were placed over phosphorus pentoxide to dry, being weighed at intervals. Seventy-five gram samples were used. The samples were placed in crystallizing dishes all of them being placed in the

same desiccator to insure their drying under uniform conditions. The results obtained are shown in Table II, and on Plate I.

A second series of determinations was then made by placing weighed samples of precipitated silica (air-dry), over different concentrations of sulfuric acid. The desiccators in which the samples were subjected to the vapors of the sulfuric acid solutions were themselves placed in a large oven, electrically heated. Under these conditions the effect of temperature and vapor pressure on the film could be studied simultaneously.

TABLE II.

Loss in Weight of Air-dry Material Placed Over Phosphorus Pentoxide.

Time in hours.	Ottawa sand.	20-mesh sand.	40-mesh sand.	60-mesh sand.	Ignited silica.	Unignited silica.
1 <sup>5</sup> / <sub>6</sub>	0.2	0.18	0.12	0.09	0.05	0.05
3 <sup>5</sup> / <sub>12</sub>	0.34	0.32	0.23	0.15	0.07	0.06
4 <sup>11</sup> / <sub>12</sub>	0.48	0.45	0.34	0.24	0.10	0.08
6 <sup>1</sup> / <sub>4</sub>	0.65	0.62	0.48	0.33	0.14	0.11
7 <sup>3</sup> / <sub>4</sub>	0.85	0.80	0.63	0.43	0.19	0.14
10 <sup>1</sup> / <sub>2</sub>	....	....	....	0.63	0.28	0.18
11 <sup>1</sup> / <sub>2</sub>	....	....	....	0.72	0.31	0.20

Results expressed in milligrams.

TABLE III.

Variation in Weight of Air-dry Silica when Temperature and Vapor Pressure are Varied.

Series 1.

12% Sulfuric Acid.

Temperature, C°.	Vapor pressure.	Increase per gram.
50	88.0	0.00408
43	61.3	0.00540
33	34.5	0.00729
19	13.6	...

Series 2.

44% Sulphuric Acid.

50	48.3	0.00242
43	33.7	0.00257
33	18.8	0.00267
19	8.0	0.00304

Series 3.

52% Sulfuric Acid.

50	31.5	0.00040
43	22.0	0.00080
33	13.3	0.00090
19	5.5	0.00150

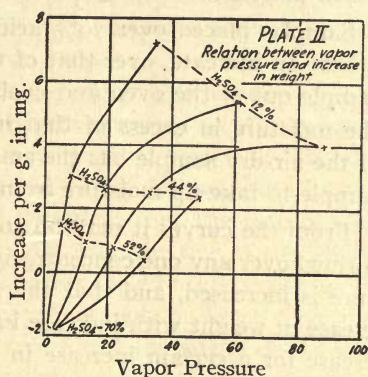
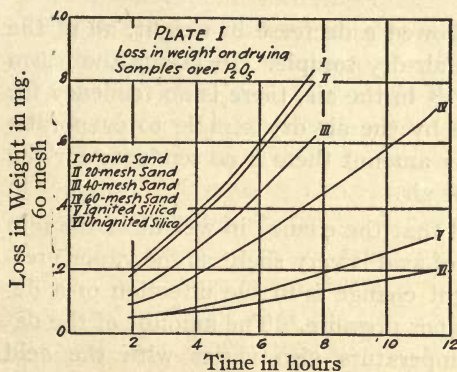
Series 4.

70% Sulfuric Acid.

50	5.9	—0.00170
43	4.3	—0.00180
33	3.0	—0.00180
23	1.6	—0.00170



On removing a sample from the oven for weighing it was allowed to cool to room temperature in the air. Since the sample was at a higher temperature than that of the room no accumulation of moisture could take place on it from the air, and any loss of moisture by it to the air would of necessity be considered as condensed moisture, and not as a part of the surface film. Reheating was continued at the same temperature until a constant weight was obtained. If the weight of the sample so treated is greater than the weight of the air dry material some moisture has been taken up which is not lost during cooling. This moisture may be considered as a part of the semi-permanent film on the surface of the grain.



If on the other hand the material on exposure to the air reverts back to the weight of the air-dry sample no thicker film than that present on the air-dry sample can be formed at that temperature. Vapor pressures greater and less than those of the air under ordinary conditions were used so that a tendency to revert to the air-dry weight could be checked from either side. The values obtained are shown in Table III, and on Plate II.

**Discussion of Results.**—When a pile of small particles like any one of these samples is exposed to conditions favoring evaporation of the surface film of moisture, the greater part of the moisture must evaporate by way of the air spaces between the particles composing the pile. If the particles are of the same shape and if the same arrangement of particles holds in the different piles, the size of the air spaces will be determined by the diameter of the particles. It might therefore be assumed that there would be a direct relation between the size of particles and the rate of evaporation. The results in Table II and the curves on Plate I show that the relationship holds for the materials used, the loss during a given interval decreasing as the grain size decreases. The relationship is not a simple one, however, since the capacity possessed by a surface for holding a liquid film, as well as the arrangement of particles in the piles may differ. That

the relationship is not simple for the three samples of meshed sand is probably due to the irregularity of the grains and the resulting irregular arrangement of them in the pile.

The results from the second series of determinations are shown graphically on Plate II. Solid lines connect points at the same temperature, while broken ones connect those for the same vapor pressure. No attempt was made to definitely determine either the shape of the curve or the actual amount of liquid held, since the purpose of this part of the work was only to get the magnitude of the change caused by variation of temperature and vapor pressure.

Samples placed over 70% acid showed a decrease in weight, all of the others an increase, over that of the air-dry sample. In taking the warm sample out of the oven and cooling it in the air, there is no tendency for the moisture in excess of that held by the air dry sample to evaporate. If the air-dry sample has the smaller amount there is no tendency for the sample to take up moisture from the air.

From the curves it may be noted that the change in weight of the film formed over any one concentration of acid is very slight as the vapor pressure is increased, and that the slight change is in the direction of a decrease in weight with increase in vapor pressure. The amount of the decrease for a certain increase in temperature also varies with the acid strength, being greater with the lower concentrations. This is equivalent to saying that the decrease for a certain temperature change is greater as the vapor pressure is greater.

Heating the sulfuric acid container would have two effects. It would decrease the capacity of the solid for holding moisture, and it would increase the amount of vapor present in the air and available for the formation of a film. The effect upon the solid would undoubtedly result in less liquid being held. Increasing the vapor present might cause either an increase or a decrease in the amount of liquid held, depending on the intensity of the force which holds the film to the solid. As the vapor pressure increases water will evaporate from the sulfuric acid solution and may evaporate from the film already present on the surface of the pearl also. In the experiments above, the resultant of the two effects brought about a slight decrease in weight as the temperature increased.

The results indicate that the thickest film that can form is formed when the temperature is low and the vapor pressure high; also that the amount held gradually decrease as the vapor pressure increases with rise of temperature. While the results shown do not make this a certainty, they do make it probable, since the only other possibility lies in the curve for one strength of acid (broken line curve of Plate II), showing a maxi-



mum at some temperature below 19° and decreasing again for vapor pressures below this maximum.

The curves indicate quite clearly that the film is not chemically combined, since the amount of liquid held at constant temperature, decreases with the vapor pressure of the sulfuric acid solution. This is not a normal behavior for chemical compounds, which lose their water, if the reaction is a reversible one stepwise, rather than at a gradual rate.

These results show roughly the magnitude of the change when a part of the film ordinarily present is removed by drying, and also the effects that may be expected if temperature or vapor pressure changes.

The results as obtained were so small that it seemed impossible to get measurable results on pearl samples of known surface. A few trials showed that the weight of pearls used would have to be at least 150 grams, and that this weight would considerably increase the time required to obtain equilibrium conditions. The fact that the loss in weight varied with the size of the grain was used as a basis for a new method of determining surface.

It will be seen from the work already described that the rate of loss of moisture from a mass of sand grains varies with the size of the grain, and that the larger the grain the greater the loss for any interval of time. It seemed probable that the loss was dependent only indirectly on the grain size, the direct factors being the amount and the shape of the unoccupied space. King<sup>1</sup> in his investigation of the flow of water through soils determined the amount of this space for different soils, calling it "pore space." The following formula was used in determining it:

$$P = \frac{Vd - W}{100Vd}$$

in which,

V = volume of sand and pore space,

d = density of sand,

W = weight of sand used,

P = pore space.

For rounded grains it was found to vary with the size of the grain, between 32% and 40% and for ordinary soils between 32% and 47%.

The force which holds the liquid in the spaces existing in a mass of small grains is physical in its nature. The nature of the surface of the grain and the size, shape and arrangement of the pores in the mass, determines the magnitude of the force. For material of the same kind the nature of the surface need not be considered.

If spherical grains of uniform size are used, and if they are arranged as compactly as possible, both the pore space and the liquid held in it are constant in amount. The rate of loss of this liquid should depend on the

<sup>1</sup> *Loc. cit.*

size, shape and arrangement of the pores. If each sample is made up of spherical grains of one definite size it seems probable that the shape of the pores would be the same in every sample and that the size of the pores would vary with the size of the grain composing the sample. It also seems probable that the arrangement of the pores would be the same. Whether this is true or not there is a relationship between the size of the grain, the pore space and the rate of loss of liquid from the pores; and spherical grains which pack so as to give a constant pore space should give results which would show this relationship most definitely.

If it is possible to determine how the rate of loss varies with the diameter of the pearl and with the pore space, the pore space can be calculated and the diameter, that is the effective diameter, of the grain can be determined from the rate of loss of liquid. For spherical grains the actual diameter would be determined, for other shapes the effective mean diameter from which to calculate the surface.

The glass pearls and Ottawa sand already described provided just the kind of material needed for determining this relationship. The centrifuge at once suggested itself as a medium by which the liquid could be removed and a method involving its use was devised.

TABLE IV.  
Losses per Gram of Sample on Centrifuging.  
Ottawa Sand.

Time in mins.	Sample No. 1.	No. 2.	No. 3.	No. 4.
10	0.0081	0.0087	0.0083	0.0084
10-20	0.0070	0.0088	0.0093	0.0073
20-30	0.0082	0.0090	0.0085	0.0080
Pearls No. 10.				
10	0.0080	0.0065	0.0064	0.0083
10-20	0.0064	0.0078	0.0062	0.0070
20-30	0.0057	0.0061	0.0050	0.0059
30-40	0.0056	0.0059	0.0050	0.0055
Pearls No. 8.				
10	0.0040	0.0039	0.0046	0.0045
10-20	0.0043	0.0054	0.0042	0.0052
20-30	0.0047	0.0050	0.0047	0.0049
30-40	0.0047	0.0051	0.0049	....
Pearls No. 7.				
10	0.0046	0.0042	0.0056	0.0058
10-20	0.0048	0.0049	0.0053	0.0052
20-30	0.0042	0.0046	....	0.0045
30-40	0.0045	....	....	....

**Method Used.**—Porcelain Gooch crucibles were used to hold the samples while they were being centrifuged, those being chosen which had perforations too small for any of the sizes of pearls used to pass through. They were as nearly the same size and shape as could be obtained. A



weighed sample of pearls was transferred to a Gooch crucible and distilled water was added to cover the sample. The sample was kept covered with water while 100 cc. of water was passed through the pearls. This was done in order to wet the pearls uniformly and to remove bubbles of air. The greater part of the free liquid was then removed by suction, the Gooch crucible was transferred to the centrifuge and the sample was rotated for ten minutes at the rate of 1000 revolutions per minute. The crucible was then removed and weighed and alternately centrifuged for a ten-minute period and reweighed until the original weight was obtained. The weights of duplicate samples as well as those of the different sizes were varied somewhat to see whether an appreciable effect on the loss in weight would result.

Ottawa sand and pearls Nos. 10, 7 and 8, were used, the loss in liquid being determined for ten minute intervals with four samples of each. The results are given in Table IV.

**Discussion of Results.**—In considering this method of determining the diameter experimentally there were five factors which, it was thought, might cause results to vary.

**1. Size and Shape of Crucibles.**—It was possible to select crucibles which were of practically the same diameter and height. This source of error was, therefore, of but very little importance. There is no doubt that a difference in the diameter of the crucible would cause the weight loss to vary, since the centrifugal force acts over the section of the crucible.

**2. Number and Size of Perforations in the Crucibles.**—No effort was made to measure accurately the size and number of perforations in the base of the Gooch crucibles. It seems probable that they would have an influence on the rate of loss of liquid unless they were numerous enough to readily take care of all of the water driven from the pearls during a ten-minute period. Apparently such differences as existed had no effect on the relative rate of loss of liquid.

**3. Amount of Water Present when Centrifuging Began.**—A rough attempt was made to adjust the amount of liquid when centrifuging began, through the application of suction for a definite time, following a definite preliminary treatment. The method used did not do this with any accuracy since the amount of liquid held by any one sample of pearls was not the same in any of the four determinations made. It was expected that this might lead to larger losses particularly during the first period of rotation. That it had no such regular effect can be seen from the results. This is probably due to the fact that on centrifuging a constant pressure is applied to the pearls from the surface layers down, and this pressure effects the removal of a certain quantity of water at the bottom, independent of the amount of water actually present in the crucible. It was found

that after the first centrifuging the top layers of pearls were practically dry, and as centrifuging was continued the dry layer deepened until all of the water was removed.

4. **System of Packing the Pearls.**—There are innumerable possibilities in arrangement when a mass of small pearls are poured into a crucible, and the pore space may vary greatly with the method of packing employed. It seems probable that the greater part of the variations found in the above results are due to this factor. The centrifugal force applied for drying purposes was the means used in these experiments to control the method of packing. The results, especially during the last two periods of rotation show that the system of packing in duplicate samples must have been closely the same.

5. **Variation in Weight of Sample Centrifuged.**—The weights of samples taken were purposely varied slightly to see whether any change in the rate of drying would result. The rate of loss on drying was found to be fairly constant for the same sample and such variations as were found did not correspond to the variations in the weight of the sample.

**Losses per Gram** (see Table IV).—The loss per gram during a ten-minute period of centrifuging while showing some variation are fairly close. Occasional high and low results occur particularly during the first two ten-minute periods. It was considered that drying conditions would be more uniform for the third ten-minute period when a layer of dry pearls covered the wet ones and when any moisture on the inside of the crucibles and above the top layer of pearls would be removed. For this reason the values obtained in this interval were used in the calculations.

It is readily seen that the loss on centrifuging any one sample is proportional to the time of centrifuging, as would be expected.

TABLE V.  
Data for Centrifugal Samples.

Sample.	Diameter.	Av. Loss per gram.	Vol. per gm. (in cc.)	% pore space.	Pore space (in cc.)	K.
Ottawa Sand.....	0.079	0.0084	0.59	36.26	0.22	0.136
Pearls 7.....	0.054	0.0044	0.45	34.00	0.15	0.128
Pearls 10.....	0.046	0.0057	0.60	33.40	0.20	0.136
Pearls 8.....	0.041	0.0048	0.49	34.20	0.17	0.140

A relation was found to exist between the diameter of the pearls, the rate of loss and the pore space. Diameters were obtained by the count-weight method, the rate of loss experimentally by centrifuging, and the pore space by calculation from King's formula. A tabulation of the data is given in Table V. The rate of loss was found to vary as the square root of the diameter and as the pore space. Expressing this in the form of an equation we have



$$L = KPD^{1/2},$$

in which,

L = loss per gram,

P = pore space, and

D = the diameter.

Values of "K" are shown in Table V. The variations in "K" indicate a variation of about 0.002 cm. in the diameters obtained.

No application of this method was made to samples of irregular shapes, since there is no method for getting a standard for the effective diameter. No. 7 was composed of pearls of two sizes which accounted in part for its smaller amount of pore space. The sample also shows a low value for "K."

While the results obtained show the relation anticipated they do not give the desired degree of accuracy. A part of this failure is no doubt due to the method of calculating pore space. It must also be noted that the value of "K" as given is limited to the crucibles used, since the loss per gram could be decreased by decreasing the number of perforations in the bottom of the crucible. Neither pore space nor diameter would be effected by this, so that "K" would have to vary if the relationship held.

The method as developed gives a general relationship but does not permit of determining the individual factors in the equation with an accuracy sufficient to warrant its application in determining diameters more closely than 0.002 cm. This variation is too large for the diameters considered. As a result of this no additional work was done along this line.

## MEASUREMENT OF THE THICKNESS OF FILM FORMED ON GLASS AND SAND.

### Introduction.

A large amount of work has been done up to the present time on the formation of a film on the surface of glass or silica, in which water has been used as the liquid to produce the film. Thus, Ihmori,<sup>1</sup> Parks,<sup>2</sup> Briggs,<sup>3</sup> Katz,<sup>4</sup> and Langmuir,<sup>5</sup> give values for the thickness of the film formed on glass, silicate or quartz surfaces.

There is a considerable difference in the values obtained as might be expected, since the materials used differed considerably in chemical com-

<sup>1</sup> *Wied. Ann.*, 31, 1006 (1887).

<sup>2</sup> *Phil. Mag.*, [6] 5, 517 (1903).

<sup>3</sup> *J. Phys. Chem.*, 9, 617 (1905).

<sup>4</sup> *Proc. Acad. Wetenschappen*, 1915, p. 445.

<sup>5</sup> *J. Am. Chem. Soc.*, 38, 2221 (1916).

position and nature of surface. A part of the material was in the form of small grains (sand and quartz), some being relatively coarse and some extremely fine powder. The glass used was in the form of thin sheets, in some cases curved (spherical), and in others plane. Each of these factors would have an influence on the thickness of film obtained, as would also the temperature and vapor pressure at which the film was formed. Some typical results obtained for the film thickness are given in the following table:

TABLE I.—FILM THICKNESS VALUES.

No.	Nature of material.	Film thickness.	Investigator.
1.	Glass globes.....	0.0000033	Ihmori
2.	Cotton silicate (glass wool).....	0.0000133	Parks
3.	Sand (microscopic powder).....	0.00000045	Briggs
4.	Quartz (very fine powder).....	0.0000013	Katz
	Anorthite (as above).....	0.0000062	Katz
5.	Glass (incandescent lamp globes).....	0.00000166	Langmuir

There are two theories regarding the formation of a film on a solid. According to the first the force acting is physical in its nature, and the intensity of its effect varies inversely as some power of the distance between the two molecules concerned. The force is similar to the force of gravitation but acts through the distance between molecules. According to this theory successive layers of molecules may be built up on the surface of a solid to a thickness such that the attractive force of the solid just equals the tendency of the outer layer of the film to evaporate.

The second theory assumes that a chemical reaction takes place and that the water taken up becomes a part of a more or less stable chemical compound. According to this theory a variable amount of water could be taken up by solids depending only on the capacity of the solid to form a loose compound with it.

The second theory has usually been assumed to hold for the film of water forming on glass surfaces, free or loosely combined alkali present in the glass, being the substance with which the water reacts. Ihmori,<sup>1</sup> found that keeping the glass in boiling water for some time decreased the amount of water which it would take up. He believed that alkali was removed during this boiling, and that the decrease in the amount of moisture taken up was due to this fact.

It seemed worth while to check the values obtained using glass and sand, having known surfaces, if possible. Since no work had been done to determine the thickest film which can form without free liquid appearing, a method of doing this was worked out. This film was compared with the film formed with other liquids to see whether there was any basis for the theory that a chemical compound formed with water.

<sup>1</sup> *Loc. cit.*



### Materials.

**Solids: Sand.**—Ordinary river sand was used. It was treated with conc. hydrochloric acid until no test for iron was shown. The acid was then washed out with distilled water and the sample dried in the air. Four samples were obtained by sifting. The first sample contained all of the sand which passed the 10-mesh screen but was retained by the 20-mesh screen. The second, third and fourth samples consisted of the fractions from the original lot retained by the 40-, 60- and 80-mesh screens, respectively. These are called 10-, 20-, 40- and 60-mesh sands in this paper.

The grains in this lot of sand were far from spherical, no two diameters being the same. An approximation of the surface was obtained by weighing a counted number of grains (4000 to 5000), to get the average weight per grain, and determining the specific gravity. On the assumption that the grains were spherical the diameter and surface of a single grain could be calculated. It was realized when these values were obtained that they were at best only approximations.

**Ottawa Sand.**—A single sample of sand called in this paper "Ottawa Sand," consisted of well-rounded grains. This sample gave values by the above mentioned method which were very close to the true value for the diameter and surface. It was considered to be of known surface.

**Glass Pearls.**—The glass pearls used were solid, round and of various sizes, as indicated in the table below. A few, which were poorly formed, were removed from the lot by rolling them down an inclined board. Those which were not round could be easily picked out in this way. The pearls were from two different sources, and apparently of different kinds of glass. They differed considerably in specific gravity.

The first lot was purchased at retail. The material was sold under the name of "Glistening Dew" and was used to decorate fancy cards. Two samples were obtained from this lot by "elutriation." A quantity of the pearls were placed in a tube and delivered from it at a slow rate into a rising column of water. Under these conditions by properly regulating the current, the lighter ones were carried up and the heavier ones sank to the bottom. These samples are No. 9 and No. 10, in the tables.

The second lot consisted of 5 samples, Nos. 1, 3, 5, 7, and 8. The individual pearls in each sample were of the same diameter except for No. 7 which contained pearls of two sizes. These samples were obtained from Germany and when received were coated with dye.

All of the samples were cleaned by boiling in conc. nitric acid, washing free from acid and air drying. The diameter, surface and volume of the pearls in each lot were determined by the method used for the sand.

**Liquids.**—Distilled water and a series of organic liquids were used to form the films.

**Specific Gravity of Solids.**—The specific gravity of the sand and the pearl samples was determined by displacement of water. A specific gravity bottle was weighed, empty, full of water, and then with a known weight of sample substituted for a part of the water. To avoid air bubbles, the weighed sample was run into water in a fine stream. The bottle was then placed in a partial vacuum and let stand for several hours before the final filling and weighing was done.

**Method of Determining Film Thickness.**—In most of the previous work done on determining film thickness, the film has been formed by subjecting the sample to the vapors of water and establishing an equilibrium at the contact surface. Usually the water vapor was at or near its saturation point. As a check on the results obtained in this way, the method used in this paper was evolved, which consists in getting an equilibrium of the film, by the use of liquid water rather than vapor, and getting it with the air saturated. This would give the maximum film which could form, and at the same time, would, by the magnitude of the results obtained, indicate whether there was an essential difference between a film formed from the vapor and one formed from the liquid.

Considering the sand and pearl samples already described, the method involves the addition of small amounts of liquid to them, thus gradually building up on them a film of water. As successive layers of molecules are added to this film a thickness is finally reached at which the surface molecules act as normal molecules. That is they evaporate, flow, exert surface tension, etc. Any liquid beyond this amount would remain in the liquid condition. It was only necessary to get a definite test for the point at which these new properties exhibit themselves.

**Apparatus.**—The first and simplest arrangement used for this purpose consisted of a buret and an Erlenmeyer flask. The weighed sample of sand was placed in the flask and liquid added from the buret a drop at a time, with thorough shaking between, until a final drop caused the grains to stick to the flask. When this occurred water was present as free liquid. This "sticking point" was taken as the end-point of the titration.

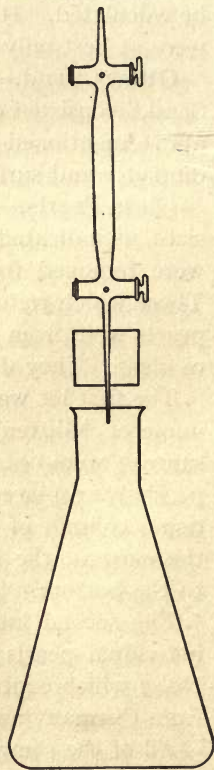


Fig. 1.

An ordinary buret soon proved unsatisfactory for delivering the liquid, especially so in cases where the liquid was volatile. Delivering the



liquid into an open flask also introduced errors with these liquids. To avoid these losses due to volatility of the liquids, and to limit definitely the volume of air saturated during a titration, a weight buret, Fig. 1, was substituted for the ordinary buret and the liquid was delivered into a closed flask.

**Procedure.**—In carrying out a single determination the following procedure was used: 200 g. of the air-dry sample was weighed and transferred to the clean, dry, Erlenmeyer flask. The flask was then closed by means of the stopper carrying the weight buret. The liquid was run in a drop at a time, the sand being thoroughly shaken after the addition of each drop. Toward the end of the titration only fractions of a drop were added, these being removed by tipping the flask to bring the pearls in contact with the tip of the buret.

A final addition of liquid caused a large number of the pearls to stick to the walls of the flask. The weight of the liquid used gave the amount of liquid taken up when a film of maximum thickness formed. Corrections were made in the case of volatile liquids for the amount of liquid necessary to saturate the air in the flask under the working conditions.

After a determination in which sand was used the sand was air-dried and then heated to strong redness in a large platinum dish. After partial cooling it was transferred to a desiccator over phosphorus pentoxide, and kept for future determinations. The pearl samples were not ignited. They were boiled with strong nitric acid, to which some hydrochloric was added and were air-dried after being washed free from acid.

This procedure was followed for the purpose of determining whether a chemical reaction was involved in the holding of the liquid. If the pearls were air-dried, there would be much less tendency for an unstable chemical compound to be broken down, than if they were dried *in vacuo*. The intention was to have the chemical compound, if it formed at all, present at the time of titration, and not formed during it. It seemed improbable that any chemical compound formed by the method used, would decompose on exposure to ordinary conditions of temperature and pressure.

**Experimental.**—In order to obtain the relationship between surface and amount of liquid to produce sticking, a series of determinations was conducted using the glass pearls, water being used as the titrating liquid. Under these conditions the only variables were those of the solid, including the nature of the surface, the size and the specific gravity of the pearls. For samples from the same source no difference in the nature of the surface was to be expected.

During the whole of this work an attempt was made to find other material suitable for titration and of known surface. Results with this material would permit conclusions to be drawn regarding the capacity

of different surfaces to hold liquid films and would thus show the effect of the other variants. No other material was found that could be used in this way.

**Reproducibility of Results.**—The apparatus as used was subject to some error due to the fact that the quantity of liquid added could only be controlled by opening the lower stopcock of the weight buret. To give an idea of the accuracy obtainable with this apparatus, a series of results obtained with each of two liquids is included. The remaining liquids gave results correspondingly accurate.

Liquid.	Water.	Nitrobenzene.
Sample.....	200 g. pearls No. 8	200 g. pearls No. 3
Weight of liquid, grams.....	0.119	0.040
	0.119	0.041
	0.117	0.039
	0.116	0.042
	0.120	0.042
	0.121	0.038
	0.116	
	0.118	
Average.....	0.118	0.040
Greatest variation from average.....	0.003 = 2.5%	= 5%
Variation between highest and lowest values	4.2%	10%

The per cent. error introduced depended principally on the amount of surface titrated or on the amount of liquid added, the greatest variation amounting to from 0.004 to 0.006 g. of liquid.

The results obtained and the calculations of film thickness are given in the accompanying table:

TABLE II.—TITRATION VALUES USING WATER.

Sample. Pearls.	Diameter in cm.	Surface sq. cm./g.	Sp. gr.	Weight.	Titration liquid per g.	Film thickness.
No. 1.....	0.1367	14.67	3.101	0.003988	0.000190	0.0000129
No. 3.....	0.1180	17.09	3.090	0.002626	0.000218	0.0000128
No. 5.....	0.0808	24.03	3.079	0.000853	0.000303	0.0000126
No. 7.....	0.0542	35.46	3.125	0.000261	0.000402	0.0000113
No. 8.....	0.0410	46.40	3.069	0.000121	0.000595	0.0000128
No. 9.....	0.0540	44.93	2.505	0.000206	0.000297	0.0000066
No. 10.....	0.0460	53.14	2.496	0.000122	0.000375	0.0000070
SANDS.						
Ottawa.....	0.0790	28.58	2.656	0.000686	0.000374	0.0000130
10-mesh.....	0.0494	46.00	2.643	0.000168	0.001310	0.0000285
20-mesh.....	0.0430	52.28	2.646	0.000110	0.001120	0.0000214
40-mesh.....	0.0280	81.90	2.650	0.000030	0.001100	0.0000135
60-mesh.....	0.0170	129.57	2.666	0.000007	0.001480	0.0000114

**Discussion of Results.**—The liquid required for a titration may be used to form a uniform film of liquid over the surface of the pearls up to



the thickness at which flow would occur. If this is the case a negligible amount of liquid would be required actually to support the grains, this amount being added after the uniform film had been added, and "sticking" would result from a concentration of this added amount at the contact surface of flask and pearl through the action of capillary forces.

On the other hand, the whole amount of liquid required may be necessary to support the pearls through the action of surface tension. In this case no film would form but all of the liquid added would concentrate at the contact surface, and "sticking" would occur as soon as the surface tension was sufficient to support the pearl.

In order to determine which of these two hypotheses held or whether the amount used in titrating was the resultant of both effects, some calculations were made of the amount of liquid necessary to support a single grain. Fig. 2 will explain the letters used and the method of calculation followed.

Consider a pearl weighing 0.0001 g., held to the surface of the flask by surface tension. The liquid holding the pearl may be considered as occupying a volume represented in section by (OBCED), the lowest level of this volume being the circumference of a circle whose radius is  $a$ . Surface tension may be considered as acting along this circumference. If the surface tension and the weight supported by it are known, the length of

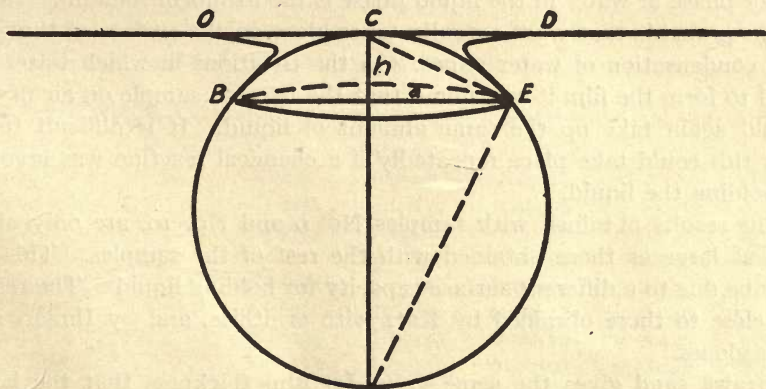


Fig. 2.

the circumference required to support the pearl is given  $0.0001/\text{sur. ten.}$  Substituting actual values and placing the quotient equal to the circumference of a circle enables one to calculate the value of  $a$  in the same units as are used for expressing the surface tension (cm.). Having the value of  $a$ , the value of  $h$  (thickness of liquid acting) may be calculated, since by geometry,

$$h : a :: a : (2R - h),$$

and all of the terms except  $h$  are known.

Knowing both  $a$  and  $h$ , the volume of liquid holding the pearl can be estimated. It was assumed that the volume of liquid necessary to support the pearl would be that required to half fill the volume represented on the figure by (OBED). This is believed to be in excess of the actual amount needed. Calculating this value for the smallest pearl used, one weighing 0.00012 g. gave 0.037 cc. per g. of pearls. Calculating the same value for pearls No. 1, the heaviest pearls used, gave 0.08 cc. per g. of pearls. These amounts are negligible when the amounts required for a titration are considered. This shows clearly that although the end-point is marked by the appearance of "sticking," which is a surface-tension effect, surface tension itself cannot account for the liquid required for a titration.

The amount of liquid required is directly proportional to the surface, and the film thickness is uniform for the same kind of glass.

As to the actual thickness of film found, it is of the same order as that found by earlier investigators who worked with the vapor phase of water in forming the film. The results are higher than those of all except Parks. It does not seem probable, in view of the results obtained, that there is any difference in the nature of the film itself, whether water in the vapor phase or water in the liquid phase is used to form the film. It also seems probable that what actually takes place on the surface of the grain is a condensation of water vapor. In the titrations in which water was used to form the film it was found that the titrated sample on air drying, would again take up the same amount of liquid. It is difficult to see how this could take place repeatedly if a chemical reaction was involved in holding the liquid.

The results obtained with samples No. 9 and No. 10, are only about half as large as those obtained with the rest of the samples. This can only be due to a different surface capacity for holding liquid. The results are close to those obtained by Katz with ornithite, and by Ihmori with glass globes.

Ottawa sand gives the same value for film thickness that the larger series of pearls does. It seems probable that this is a chance agreement, since the surface of the sand differed considerably from that of the pearls, both in hardness and in texture.

As a whole the results indicate that there are two factors which influence the amount of liquid necessary to form the maximum thickness of film. The first factor is the amount of surface, the actual area that the film must cover. The second is the nature of the surface itself, its capacity to hold a film.



Not a great deal is known regarding the variants which determine the capacity factor of a surface. It is probably related to the free energy present in the atoms of the surface layers.

The work up to this point indicated that the film thickness should be independent of the liquid used, providing the liquid is not too viscous to spread readily. It also indicated the desirability of applying the titration method to the determination of the surface of irregular particles like sand grains.

For the purpose of obtaining surface values for the meshed sands, complete titrations for each of these samples with water and with each of the organic liquids was carried out. An attempt was made also to titrate finer sands, 100-mesh, 150-mesh, 200-mesh. These however, would not permit of an even distribution of the liquid over the surface, and no satisfactory titrations were obtainable.

To determine whether the same thickness of film would be found with a different liquid, titrations were carried out first with the pearls and then with the sands making use of the organic liquids. The determinations with the pearls were not completed when they were found to check closely for the first liquids used but those on the sands were completed for all of the liquids.

The organic liquids used were chosen so that the specific gravity, volatility, surface tension, etc., varied.

The results obtained from these two series of titrations are given in Table III, and will be discussed together.

TABLE III.—TITRATION VALUES FOR SANDS AND PEARLS WITH ORGANIC LIQUIDS.

Liquids.	Sands.				
	10-mesh.	20-mesh.	40-mesh.	60-mesh.	Ottawa.
Nitrobenzene.....	0.00136	0.00117	0.00109	0.00148	0.00039
Water.....	0.00133	0.00108	0.00112	0.00151	0.00037
Aniline.....	0.00122	0.00107	0.00109	0.00148	0.00039
Dimethylaniline.....	0.00131	0.00108	0.00107	0.00155	0.00039
Phenyliodide.....	0.00126	0.00112	0.00112	0.00149	0.00039
Toluol.....	0.00134	0.00116	0.00110	0.00146	0.00038
Turpentine.....	0.00131	0.00116	0.00108	0.00142	0.00039
Pyridine.....	...	...	0.00109	...	...

Liquids.	Pearls.					
	No. 1.	No. 3.	No. 5.	No. 8.	No. 9.	No. 10.
Nitrobenzene.....	0.00018	0.00020	0.00030	0.00056	0.00027	0.00040
Water.....	0.00019	0.00022	0.00030	0.00059	0.00030	0.00037
Aniline.....	...	...	...	0.00055	0.00023	0.00039
Dimethylaniline ...	0.00017	0.00022	0.00032	0.00059	0.00029	0.00045
Phenyliodide.....	0.00018	...	...	0.00059	0.00030	0.00039
Toluol.....	...	0.00021	...	0.00053	0.00031	0.00038

**Discussion of Results.**—The results show that the thickness of the film is independent of the kind of liquid used for titrating, and that the sand titrations can be checked with as good an accuracy as titrations of pearls. Occasional results vary, but the uniformity for the whole series is pronounced. This proves definitely that the surface tension of the liquid has no effect on the amount of liquid required for a titration. The surface tension of water is much greater than that of the other liquids but the volume required per gram is the same. This could not be true if the surface tension influenced the amount of liquid required to produce “sticking.”

It also proves that there is no chemical reaction in the ordinary sense of the term, when a film of water forms on glass. While it might be possible to imagine such an effect between water and glass, it is obviously impossible to do so with the rest of the liquids of the series. In addition to this the calculated film thickness for different sizes of pearls is found to be the same, showing that the volume for titration varies with the surface.

The definite conclusion can be drawn that these films are not due to the formation of a chemical compound, but that they are held by the free surface energy of the solid. It seems certain that the same force holds a thinner film.

While these films are formed by the addition of liquid to the solid, the inference is that the same conclusion may be drawn for a film formed from the vapor phase. This inference is supported by the fact that the values obtained for the film thickness when formed from the vapor phase are only very slightly lower than those formed by the addition of liquid. It seems probable that a liquid film forms in both cases, but that with the unsaturated vapor phase it never becomes thick enough to show as a normal liquid on the surface of the solid, while when liquid is used the formation of free liquid marks the end of the titration and indicates the thickest film that can form without free liquid being present.

In titrating sands a simple relationship such as was found for the pearl samples does not exist between titrated amount and calculated surface. This is partly due to error in calculating the surface, on the assumption that the grains are spherical, and partly to the fact that extra liquid is required to fill the etchings in the surface. However, if relative effective surfaces are sought they may be expected to be proportional to the titration values since there is no application of the surface which would not involve the etchings and so produce results which would be proportional to those obtained by the titration method.



### Summary.

This paper describes a new method of obtaining the thickness of the maximum film which can form on a surface without free liquid being present. Evidence is presented to show that the liquid forming the film does not combine chemically with the solid. The method has been applied to sand and to glass, and films have been formed with water and with several organic liquids. The film thickness is found to be independent of the liquid used and of the size of the solid particle. The method gives accurate values for the effective surface of sand particles, providing that surfaces of the same kind are compared.

## PART II.—THE ADSORPTION OF COPPER SULPHATE BY GLASS AND SAND.

**Introduction.**—Adsorption has been applied as a general term to include any one or a group of effects taking place at the contact surface between two different phases. In a specific case it may be a capillary effect, or an adsorption, or a chemical change. Or it may be a combination of two or more of these. The term "Adsorption" as at present used, indicates simply that the action taking place, which is always a change in concentration, is limited roughly to the surface, and is relatively small in amount.

In view of the fact that the term is used to include so many effects that may differ entirely in their nature, such as the formation of a film of liquid or gas on any solid, the accumulation of any dissolved substance on the surface of any solid, liquid, or gas in contact with its solution, etc., it is not surprising that the equation used to express the relation between adsorption and the factors which influence it, must be a general one. On the contrary, it is surprising that any equation, no matter how general, will apply to so many seemingly different processes.

The equation which is generally used<sup>1</sup> for the adsorption isotherm, and which has been found to hold for a good many individual cases, is as follows:

$$X/M = kC^n.$$

in which,

X is the amount adsorbed,

M is the mass of the adsorbing substance,

C is the concentration of the adsorbed substance,

"k" and "n" are constants depending on the materials used.

"n" may be positive or negative, whole or fractional.

<sup>1</sup> *Zeit. Phys. Chemie*, 57-425, 1906.

It will be noted that the equation as given does not include the surface factor at all, in spite of the fact that adsorption is defined as a "change in concentration of the adsorbed substance at the surface of contact." Its omission is brought about chiefly by two factors, the necessity of using very large surfaces in order to get a measurable effect, and the practical difficulties involved in the subjection of a large, known surface to adsorption.

The solid materials ordinarily used for an adsorbing surface are in a finely divided condition in order to increase the surface as much as possible, without at the same time increasing the bulk of the material used. With material of this kind it is very probable that the relation between surface and weight is constant. That is, two grams of finely ground charcoal, clay, or silica, have a surface double that of one gram of the same sample of material. In order for this to hold exactly, it is necessary to assume that the particles of the portions of the adsorbing substance used are all of the same mean size, but even without this assumption, the results obtained by substituting mass for surface would be more accurate than those based on the values of the surface derived in any other way known at the present time. In effect then, the term " $M$ ," in the equation given above is a relative measure of the surface involved.

If we view adsorption as a purely physical effect, a change in concentration without chemical reaction occurring, and produce it upon a known surface, and with a known concentration of a solute, the adsorption per unit surface should be a constant quantity. Since the same materials are used, " $k$ " and " $n$ " should have constant values, and if " $C$ " is also kept constant,  $X/M$  or  $X/S$  should give a constant value ( $S$ , represents the surface).

Much attention has been given to the solubility of glass in acid, alkali, and salt solutions, in order to determine to what extent the error introduced from this source, influences analytical results.

No attempt has been made, so far as our study of the literature reveals, to determine whether glass has a tendency to concentrate certain metallic ions or compounds on its surface, either by a process of physical adsorption, or by a double decomposition, resulting in a solution of the glass and the precipitation of the metal on the surface. It is obvious, however, that if a concentration of the solute or of one of its ions does take place on the surface of the glass, it only takes place to a very slight extent, since the exactness of quantitative procedure would reveal even small variations from this cause.

**Purpose of the Work.**—Since glass is so universally used in analytical work as a container for solutions of all kinds, it seemed worth while to attempt to measure the increase in concentration at the surface of glass,



in a specific case. The determination of the increase in concentration, or the adsorption, with a given solution, and the variation in amount adsorbed with the concentration of the solution, were both of importance.

If increase in concentration took place, it might result from causes which were purely physical, and it might result from a chemical reaction occurring at the contact surface. With pure silica a chemical reaction would not be expected. Comparative values using silica might help to decide whether, when glass is used, the adsorption is physical or chemical. It was hoped that a critical examination of all of the results obtained would lead to a definite conclusion concerning the nature of the process.

In all of the work on adsorption that has been done up to the present time, only one size of particle has been used, and the total surface exposed has been varied by increasing or decreasing the weight of this sample. The pearl samples described in the former paper afforded an adsorbing medium of known surface. The surface of the meshed sand samples was also known approximately. Both materials had shown the surface relationship when water was adsorbed. If the adsorption was purely physical, results similar to those obtained with water, in the former paper could be expected. The use of these samples also permitted us to vary the surface exposed without varying the weight of sample exposed. If the adsorption depended primarily on the surface exposed, its amount would vary as the surface varied. If other factors were involved, such as the mass of the individual particles, this surface relationship would not be found. The only objection to this material was that the size of the grains necessarily limited the surface which could be exposed for adsorption, which would result in very small adsorption values.

Copper sulfate was chosen as the substance to be adsorbed, principally because of the ease and accuracy with which the copper present could be determined. No precipitation or filtration was required, a point of very great importance when very dilute solutions are used. The adsorption of copper sulfate by glass might be either physical or chemical in its nature. Since we desired to study an adsorption which might result from either in order to distinguish between them, it fulfilled the requirements in this regard also.

**Materials.**—Pearl samples and meshed sands, as in the previous paper.

Copper sulfate solutions made up from carefully recrystallized copper sulfate.

**Method.**—The method used consisted in placing one hundred grams of the pearls in a clean dry Erlenmeyer flask. Over this was poured one hundred cc. of the copper solution. After shaking and letting stand for a definite time, ten cc. of the liquid was pipetted off and the copper present in it determined volumetrically. This was repeated at the intervals noted in the tables.

In order to be sure of the end point used, and also to check any variation in value of the titrating solution, a blank was run before and after each series of determinations. The blank consisted in the titration of a ten cc. portion of the solution being used, with no pearls present. A lower titration value for the solution taken from the pearls, than that obtained by running a blank, indicated that an adsorption had taken place.

The iodide titration method was used to determine the amount of copper present in the solution. Ammonia was added to a portion which had been pipetted off, until an excess was present, as indicated by the appearance of a deep blue color. Acetic acid was next added to acid reaction, followed by about a gram of potassium iodide. The iodine liberated was titrated with sodium thiosulfate solution, and the copper present calculated from the amount of thiosulfate required.

In titrating these dilute solutions it was found that, after the disappearance of the blue color, a light reddish violet color persisted, a few additional drops being required to cause its disappearance. The titration was continued to the disappearance of the reddish violet color, as a more definite color change occurred at that time. Checks run using the two end-points indicated that either could be used without materially effecting the results obtained. The thiosulfate solution used in titrating was standardized by means of a copper sulfate solution, prepared from pure copper foil, and diluted to a strength corresponding to that of the thiosulfate solution.

Jena glass flasks were used to hold the pearls during adsorption and were also used for the titrations. Any variations due to the use of glass flasks should be present to the same extent in the blank determinations.

**Experimental.**—A few preliminary experiments indicated that it was necessary to use the greatest care in cleaning and handling the pearls. If the adsorption was physical and reversible, placing the pearls in a current of running water for some time should remove the adsorbed material. On trying this out with precipitated silica and with the pearl samples, it was found that all of these samples retained copper. Iron was also present in all. Boiling with aqua regia and then washing with distilled water, and drying, removed both of these metals. In addition adsorption values were greatly reduced after boiling with aqua regia, showing that a great part of the effect obtained with the material as first used, was chemical in its nature.

As a result, samples subjected to adsorption were boiled in aqua regia, washed, and air-dried before being used with a second solution. Check determinations, using the same concentration of copper sulfate solution as had been used previous to this treatment showed that this method of cleaning the pearls had no appreciable effect either on the individual adsorption values obtained, or on the shape of the adsorption curve.



The results obtained are shown in the following tables (I and II). On the accompanying plates, curves are plotted based on these results. Most of the values represent an average of two separate determinations, though some of the later ones have not been so checked.

TABLE I.  
Adsorption Results.

1. Copper sulfate solution contains 0.000042 gram Cu per cc.  
Values in terms of grams Cu adsorbed from 10 cc. by 100 grams of solid.

Samples.	Amount adsorbed in			
	20 min.	4½ hrs.	29 hrs.	51 hrs.
Pearls 1.....	0.00011	...	0.00052	0.00062
Pearls 3.....	0.00010	0.00034	0.00052	0.00065
Pearls 5.....	0.00026	0.00035	0.00043	0.00059
Pearls 7.....	0.00033	0.00095	0.00155	0.00153
Pearls 8.....	0.00071	0.00073	0.00138	0.00151
Sand 40-mesh.....	0.00025	0.00019	0.00047	0.00005
Sand 60-mesh.....	...	0.00004	0.00016	0.00012
Sand 80-mesh.....	...	0.00001	0.00005	0.00004
Sand Ottawa.....	0.00005	0.00019	0.00032	0.00030
Prec. Silica.....	0.00114	0.00191	0.00191	0.00210

2. Copper sulfate solution contains 0.000113 gram Cu per cc.

Pearls 1.....	0.00028	0.00061	0.00100	0.00115
Pearls 3.....	0.00083	0.00104	0.00125	0.00131
Pearls 5.....	0.00073	0.00072	0.00070	0.00069
Pearls 7.....	0.00143	0.00226	0.00274	0.00326
Pearls 8.....	0.00122	0.00176	0.00214	0.00222
Sand 40-mesh.....	0.00028	0.00034	0.00031	0.00055
Sand 60-mesh.....	...	0.00024	0.00032	0.00023
Sand 80-mesh.....	0.00007	0.00015	0.00010	0.00017
Sand Ottawa.....	0.00004	...	0.00020	0.00022
Prec. Silica.....	0.00311	0.00512	0.00514	0.00482

3. Copper sulfate solution contains 0.000153 gram Cu per cc.

Pearls 1.....	...	...	0.00110	0.00120
Pearls 3.....	...	...	0.00150	0.00200
Pearls 5.....	...	...	0.00080	0.00100
Pearls 7.....	...	...	0.00290	0.00300
Pearls 8.....	...	...	0.00240	0.00300
Pearls 9.....	...	...	0.00040	0.00070
Pearls 10.....	...	...	0.00080	0.00090

4. Copper sulfate solution contains 0.000352 gram Cu per cc.

Pearls 1.....	0.00010	0.00030	0.00120	0.00140
Pearls 3.....	0.00020	0.00030	0.00270	0.00300
Pearls 5.....	0.00050	0.00090	0.00140	0.00160
Pearls 7.....	0.00010	0.00020	0.00370	0.00400
Pearls 8.....	0.00020	0.00080	0.00300	0.00330
Pearls 9.....	0.00070	...	0.00070	0.00100
Pearls 10.....	...	...	...	...

TABLE I (Continued).

5. Copper sulfate solution contains 0.000655 gram Cu per cc.

Values in terms of grams Cu adsorbed from 100 cc. by 100 grams of solid.

Samples.	Amount adsorbed in				
	10 min.	30 min.	2½ hrs.	24 hrs.	49 hrs.
Pearls 1.....	0.00070	0.00080	0.00100	0.00120	0.00140
Pearls 3.....	0.00210	0.00260	0.00290	0.00370	0.00470
Pearls 5.....	0.00030	0.00025	0.00040	0.00180	0.00210
Pearls 7.....	0.00070	0.00130	0.00300	0.00410	0.00470
Pearls 8.....	0.00070	0.00250	0.00280	0.00290	0.00300
Pearls 9.....	0.00020	0.00030	0.00040	0.00100	0.00140
Pearls 10.....	0.00040	0.00170	0.00280	0.00310	0.00290

6. Copper sulfate solution contains 0.00150 gram Cu per cc.

Samples.	Amount adsorbed in				
	13 min.	30 min.	3½ hrs.	24 hrs.	49 hrs.
Pearls 1.....	0.00029	0.00025	0.00028	0.00031	0.00032
Pearls 3.....	0.00018	0.00018	0.00025	0.00032	0.00032
Pearls 5.....	0.00011	0.00025	0.00032	0.00036	0.00032
Pearls 7.....	0.00018	0.00032	0.00055	0.00057	0.00083
Pearls 8.....	0.00025	0.00032	0.00032	0.00053	0.00061
Pearls 9.....	0.00016	0.00027	0.00040	0.00047	0.00047
Pearls 10.....	0.00021	0.00031	0.00032	0.00042	0.00048

TABLE II.

Adsorption Values for All Concentrations of Copper Sulfate Used.

Samples.	Amount adsorbed from concentration of					
	0.00150 gm./cc.	0.000655 gm./cc.	0.000352 gm./cc.	0.000153 gm./cc.	0.000113 gm./cc.	0.000042 gm./cc.
29 hrs.						
Pearls 1.....	0.0003	0.0012	0.0012	0.0011	0.0010	0.0005
Pearls 3.....	0.0003	0.0037	0.0027	0.0015	0.0012	0.0005
Pearls 5.....	0.0004	0.0018	0.0014	0.0008	0.0007	0.0004
Pearls 7.....	0.0006	0.0041	0.0037	0.0029	0.0027	0.0015
Pearls 8.....	0.0005	0.0029	0.0030	0.0024	0.0021	0.0014
Pearls 9.....	0.0005	0.0010	0.0007	0.0004	....	....
Pearls 10.....	0.0004	0.0031	....	0.0008	....	....
50 hrs.						
Pearls 1.....	0.0003	0.0014	0.0014	0.0012	0.0011	0.0006
Pearls 3.....	0.0003	0.0047	0.0030	0.0020	0.0013	0.0006
Pearls 5.....	0.0003	0.0021	0.0016	0.0010	0.0007	0.0006
Pearls 7.....	0.0008	0.0047	0.0040	0.0030	....	0.0015
Pearls 8.....	0.0006	0.0030	0.0033	0.0030	0.0022	0.0015
Pearls 9.....	0.0005	0.0014	0.0010	0.0007	....	....
Pearls 10.....	0.0005	0.0029	....	0.0009	....	....
30 min.						
Pearls 1.....	0.0002	0.0008	0.0003	....	0.0003	0.0001
Pearls 3.....	0.0002	0.0026	0.0003	....	0.0008	0.0001
Pearls 5.....	0.0002	0.0002	0.0009	....	0.0007	0.0003
Pearls 7.....	0.0003	0.0013	0.0002	....	0.0014	0.0003
Pearls 8.....	0.0003	0.0025	0.0008	....	0.0012	0.0007
Pearls 9.....	0.0003	0.0003	....	....	....	....
Pearls 10.....	0.0003	0.0017	....	....	....	....



**Discussion of Results.**—The results in the above tables show that a definite and positive concentration of copper takes place at the surface of the glass pearls. The adsorption is not large for any of the samples used, the maximum value being 0.00514 gram of copper adsorbed by 30 grams of precipitated silica. For glass, the maximum is 0.00470 gram of copper, adsorbed by 100 grams of pearls. One hundred grams of pearls represents 1500 sq. cms. to 5300 sq. cms. of surface depending on the sample used.

Results using the meshed sand samples are included for some of the first concentrations used. The adsorption values are small and they are very irregular. Since the surface was not definitely known, and since the results obtained were too small and too irregular to permit definite conclusions to be drawn, these samples were omitted in the later work.

The original values obtained with precipitated silica were very large. Careful washing and drying reduced the values obtained to one-third of the former value. Only thirty grams of silica could be used with 200 cc. of copper sulfate solution. The values given in the tables are for these amounts. The largest result obtained in the series was that with precipitated silica when the concentration of copper sulfate was 0.000113 gram per cc. While the result is larger than any of those obtained using pearls it is also true that the surface exposed is enormously larger. This result, therefore, really agrees with those obtained with the meshed sands, all of them indicating that the adsorption of copper from copper sulfate solution, by silica, is smaller than the adsorption of the same substance by glass.

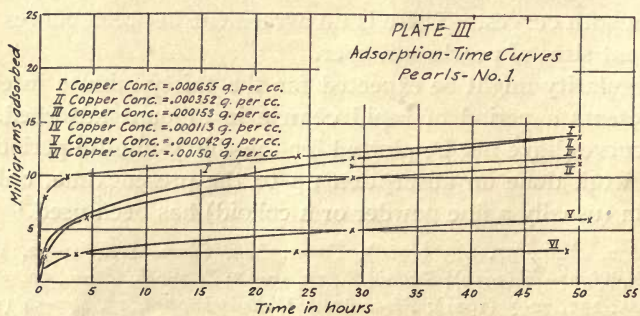
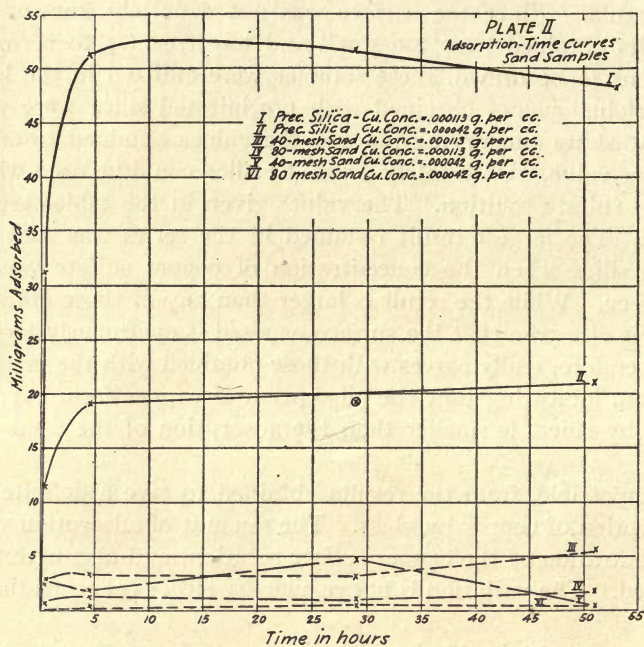
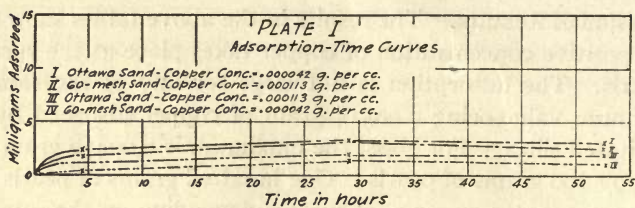
It is impossible, from the results obtained to give a definite value for the adsorption of copper by glass. The amount of adsorption varies with the concentration of the copper sulfate solution, and also with the size of pearls used. The variation is not regular for either concentration or pearl size.

Results were obtained using six different concentrations of copper sulfate. For the most part the results show good agreement. The adsorption-time curves, as well as the adsorption-concentration curves, appear as smooth curves. There is no agreement between curves representing different sizes of pearls, however.

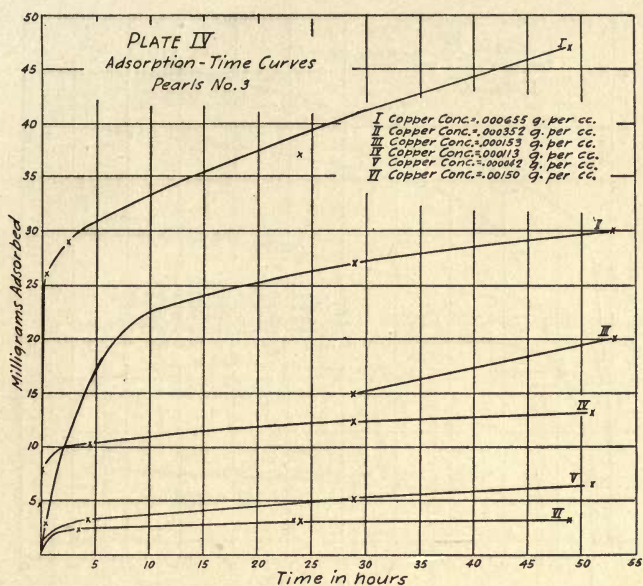
Less regularity might be expected for the thirty-minute interval, since this represents a period of rapid change in amount adsorbed. On this account curves have not been plotted for the thirty-minute period.

In the work done on adsorption up to the present time, only a single sized grain (usually a fine powder or a colloid) has been used.<sup>1</sup> With this

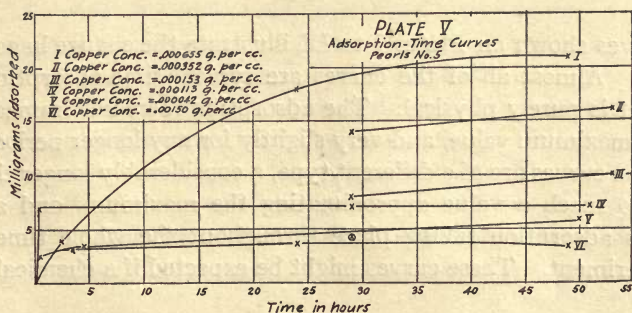
<sup>1</sup> *Z. phys. chem.*, **57**, 425 (1906); *Trans. Lon. Chem. Soc.*, **91-92**, 1666 (1907); *Biochem. Z.*, **23**, 27-42 (1910); *Kolloid Z.*, **15**, 10-18; *Z. anorg. Chem.*, **60**, 306-8 (1908); *Compt. rend.*, **151**, 72-5 (1911); *Proc. Acad. Wetenschappen*, **15**, 445-54 (1913).

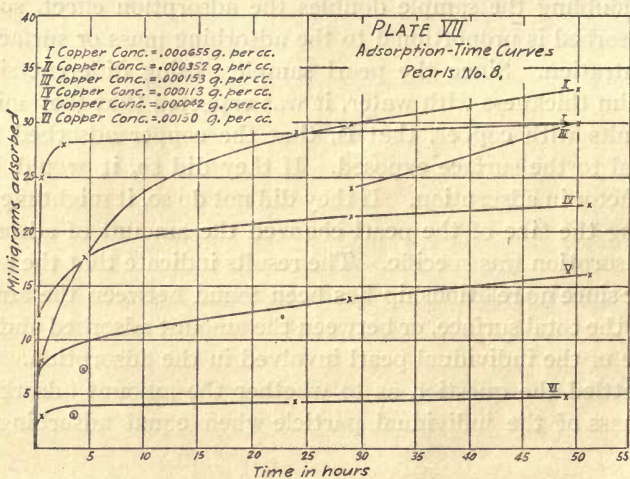
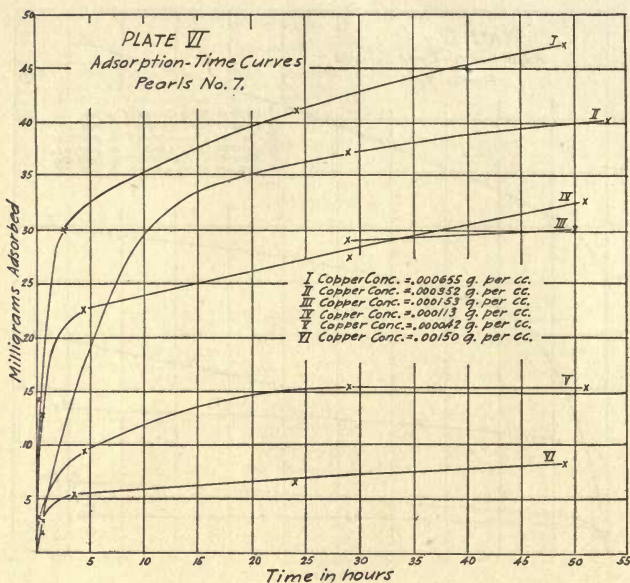






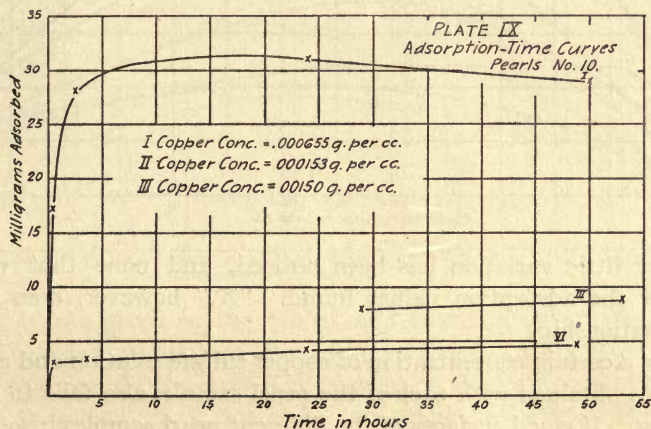
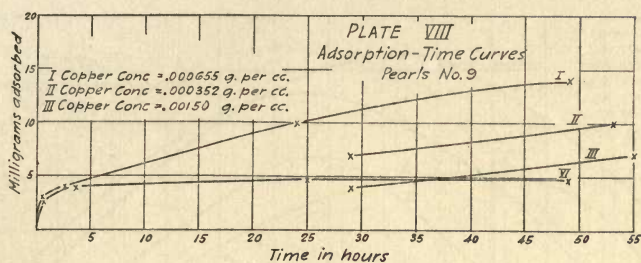
material, doubling the sample doubles the adsorption effect, so that the amount adsorbed is proportional to the adsorbing mass or surface for any one concentration. Since the pearl samples, using different sizes, gave the same film thickness with water, it was expected that they might yield similar results with copper, that is, that the copper adsorbed would be proportional to the surface exposed. If they did so, it would eliminate mass as a factor in adsorption. If they did not do so, it might mean either, that varying the size of the pearl changed the amount of adsorption, or that the adsorption was specific. The results indicate that the adsorption was specific since no relationship has been found between the amount adsorbed and the total surface, or between the amount adsorbed and the mass and surface of the individual pearl involved in the adsorption. This still leaves unsettled the question as to whether the amount adsorbed varies with the mass of the individual particle when equal adsorbing surfaces are used.





The curves shown on Plates I to IX illustrate the change in adsorption with time. Almost all of the curves are typical time-adsorption curves if the effect is purely physical. The adsorption increases immediately to almost its maximum value, and very slightly for any longer period of time. A few of the curves are of a different type, a considerably longer time being required to reach a value approximating the maximum, and a gradual increase in adsorption taking place throughout the whole time interval of the experiment. These curves might be expected if a chemical reaction



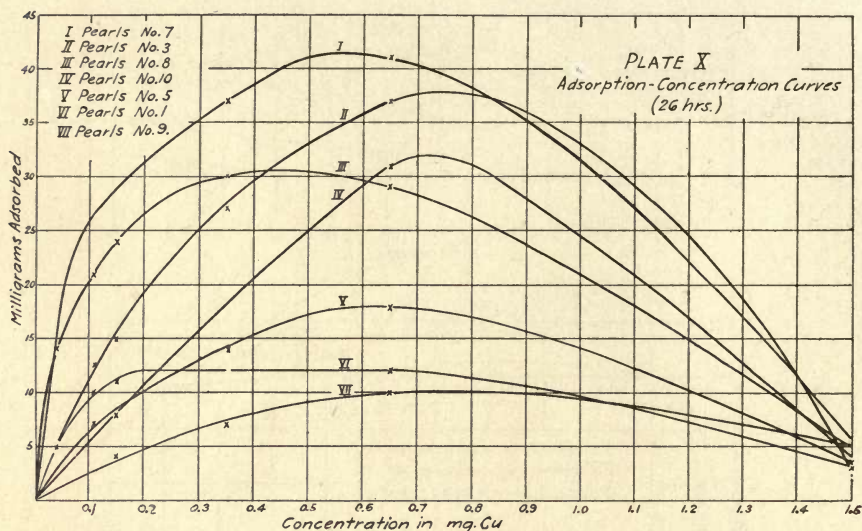


occurred at the surface of contact. The velocity of reaction would be decreased by the reaction products formed especially if they were deposited on the glass, so that a considerable time might be required to reach these maximum values.

It can be stated definitely that this latter type of curve was not due to an impurity on the surface of the samples, since curves obtained after carefully recleaning the pearls were of the same shape, the magnitude of the individual results being almost the same.

Table II shows the adsorption values obtained with each sample of pearls at each concentration of copper sulfate at the end of a definite period of contact. Consider the results obtained using any one sample, and varying the concentration of the copper sulfate solution. "M" or surface is constant. Therefore, "X" or the adsorbed amount should vary as "C" raised to some power " $n$ ." Under these conditions, "X" would increase as "C" increases if " $n$ " is positive, and would decrease as "C" increases if " $n$ " is negative. The variation in the value of " $k$ " is the only factor which would interfere with this relationship. In those cases in which the value of " $k$ " has been studied,<sup>1</sup> to determine its variation with the concentra-

<sup>1</sup> Z. Phys. Chem., 57, 425 (1906).



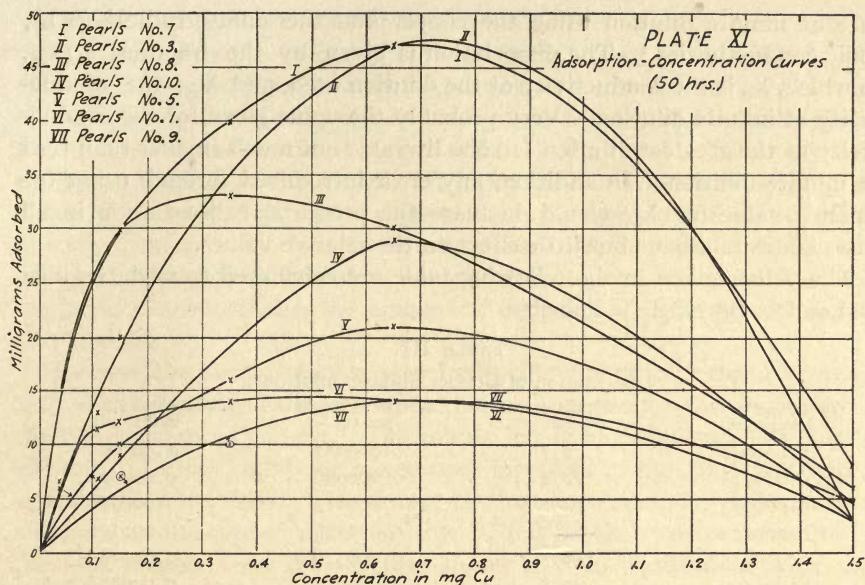
tion, very little variation has been noticed, and none that would account for the adsorption values found. "X," however, does not show either relationship.

Taking a certain concentration of copper sulfate solution and comparing the values obtained with each of the pearl samples also fails to show any regularity. If equal surfaces of the different pearl samples have the same capacity to adsorb copper sulfate, as they do for a water film, and the concentration "C" is kept constant "X" would vary as "M." " $k$ " and " $n$ " would not vary if the nature of the surface is the same and the concentration is also the same. The results do not show any relationship between "X" and "M."

It is seen from what has preceded that there is no fixed amount of adsorption of copper from solution, by glass, but that the amount adsorbed varies with the copper concentration and with the size of the pearls used. It is also seen that the results do not satisfy the adsorption isotherm, which requires a rapid increase in amount adsorbed up to a certain concentration, and a very gradual increase for greater concentrations. All of these facts indicate that we are not dealing with an ordinary physical adsorption.

The values given in Table II show a maximum adsorption for one of the concentrations used, this being in most cases the concentration 0.000655 gram Cu per cc. The curves showing this same fact are shown on Plates X and XI. While the curves on these plates are drawn as continuous curves, it should be stated that only that part of the curve to the left of the concentration, 0.000655 gram per cc. has been fixed by





adsorption values given in the tables, and that the only values to the right of this concentration are those for the concentration 0.00150 gram per cc. Consequently the part of the curves on the right side of this concentration (0.000655) may not have the shape indicated. The values with the concentration 0.00150 gram per cc. make it certain that the adsorption value does decrease at some point, and that the adsorption-concentration curve does show a maximum.

In looking through the literature on adsorption it was found that several curves of this kind were known, and that these adsorptions which showed a maximum value for a given concentration were classed as "anomalous."<sup>1</sup> In fact the same sort of an effect had already been noticed with copper sulfate when it is adsorbed by filter paper or clay.<sup>2</sup> The maximum was obtained with a 0.02 *N* solution, corresponding to 0.000638 gram Cu per cc.

If the adsorption is purely physical there are three possibilities to be considered. Copper sulfate, undissociated, may be adsorbed, copper ion may be adsorbed or copper hydroxide may be formed by hydrolysis and absorbed. If the adsorption is chemical, a reaction between copper sulfate and the glass, or some constituent of it, would result in copper being deposited on the glass surface.

The percentage dissociation of copper sulfate in solution for the concentrations used, can be calculated from the conductivity of copper sul-

<sup>1</sup> Zeit. Chem. Ind. Koll., 7, 113-28; 9, 135-6; Z. Phys. Chem., 73, 399; 62, 655.

<sup>2</sup> J. Phys. Chem., 10, 290-8 (1906).

fate at infinite dilution using the copper and the sulfate radical ( $\text{SO}_4$ ), ionic conductivities.<sup>1</sup> The dissociation is given by the fraction,  $\lambda_v/\lambda_\infty$ , in which,  $\lambda_v$ , is the conductivity at the dilution used, and  $\lambda_\infty$ , the conductivity at infinite dilution. Very probably the value given for the conductivity at the greatest dilution (10,000 liters) is not much smaller than that at infinite dilution. In addition, any error introduced through using too small a value for  $\lambda_\infty$  would increase the percentage dissociation in all cases and would have but little effect on the relative values.

The values given in the following table are calculated from data given in Landolt-Börnstein's Tabellen.

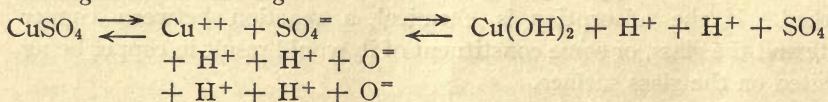
TABLE III.  
Dissociation of Copper Sulfate Solutions.

Cu. concentration grm. per cc.	Dissociation percent.	Weight Cu as ion per cc.	Weight Cu as undis. salt.
0.000042	87.7	0.000037	0.000005
0.000113	78.4	0.000089	0.000024
0.000153	74.2	0.000113	0.000040
0.000352	64.3	0.000226	0.000126
0.000655	56.5	0.000370	0.000285
0.00150	47.5	0.000612	0.000888

It is readily seen from this table that the actual amount of copper ion present per 100 cc. and in a far greater measure, the actual amount of undissociated copper sulfate, increases with the concentration of the copper sulfate solution. This has an important bearing on the adsorption.

If the copper ion were adsorbed, either the adsorption should increase in some proportion as the amount of ion present increased, or it should maintain a constant value above a certain concentration at which the surface is saturated with respect to the adsorbed substance. That is, a normal adsorption curve would be expected. There is no apparent explanation for an adsorption-concentration curve of the kind shown on the plates, if copper ion is adsorbed. The same is true if copper sulfate undissociated, or if both this and the copper ion are adsorbed.

There is, however, another possibility, without the necessity of considering ions or compounds not known to exist at present. Solutions of copper salts are known to react acid. This can be explained only by assuming that very dilute solutions of copper sulfate are hydrolyzed, according to the following reactions:



The reactions are reversible and the amount of undissociated copper hydroxide formed depends on the  $\text{SO}_4$  ion present.

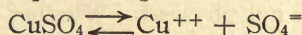
<sup>1</sup> Landolt-Börnstein Tabellen, p. 1103.



Table III gives the weight of copper ion per cc. at each concentration used, from which the weight of sulfate ion ( $\text{SO}_4$ ) can be calculated. It, of course, increases in the same proportion as the weight of copper ion.

A dilute solution of copper sulfate may, according to the reaction given above, contain undissociated copper sulfate, copper and sulfate ions, and copper hydroxide, undissociated. It is known from the values given in Table III that as the amount of copper sulfate per liter increases, the amount of copper ion and the amount of sulfate ion both increase, although the per cent. dissociation decreases. It might be expected that, at least for the lower concentrations, the amount of copper hydroxide per cc. would also increase.

However the formation of copper hydroxide differs from that of copper ion. That is, different forces are active in determining the amounts of the two substances present. The copper ion formed is dependent on the amount of copper sulfate dissolved, and increases in the same proportion as the sulfate ion does. The copper hydroxide formed also depends in a measure, on the copper sulfate dissolved, and on the relative amounts of the ions present. As the reaction shows it is in equilibrium with the sulfate ion. Consequently at some concentration, the amount of sulfate ion in solution will become great enough so that no copper hydroxide can exist, and the equation representing the solution of the salt will become:



According to this assumption the amount of copper hydroxide present in a dilute solution of copper sulfate, increases as the concentration of the salt increases, up to a certain point at which the amount of sulfate ion present, is great enough to cause a part of the copper hydroxide to dissolve. Above this concentration the amount of copper hydroxide decreases as the concentration increases.

It will be noted that the adsorption-concentration curves show the same characteristics. The amount of copper adsorbed increases with the concentration of the sulfate, up to a certain concentration. Above this concentration the amount of copper adsorbed decreases, being very close to zero at the highest concentration used (0.00150 g. Cu per cc.).

It has been impossible to get any definite data on the amount of copper hydroxide present in these solutions. A maximum is obtained, however, in the adsorption-concentration curves, and a similar maximum may be expected in the curve showing the change in concentration of copper hydroxide as the concentration of copper sulfate increases. If it is assumed that the adsorption-concentration curve is dependent on the copper hydroxide concentration curve, the shape of the adsorption curve would correspond to that found experimentally. No other satisfactory explanation has been given. Likewise, if copper hydroxide is adsorbed and the

curves are plotted using the concentration of copper sulfate as abscissae, an ordinary adsorption curve would not be expected.

It is possible, therefore, to explain the results obtained on the assumption that hydrolysis of copper sulfate takes place in dilute solution, with the formation of undissociated copper hydroxide, copper hydroxide being adsorbed. This would permit of viewing the adsorption as purely physical in its nature.

It might also be stated that the same sort of an explanation would apply to all of the cases of "anomalous adsorption" found in the literature. This type of curve is limited definitely to inorganic salts and to basic dyes, both of which are apt to be subject to hydrolytic dissociation.

It seems probable that only a slight amount of hydrolysis takes place with any of the concentrations used. Only one statement was found for the amount of hydrolysis of copper sulfate solution, and the volume employed is questionable in that case. The per cent. hydrolysis shown was 0.057 per cent.<sup>1</sup>

According to the explanation given for the shape of the adsorption-concentration curve, this adsorption must be physical in its nature consisting in a concentration of undissociated copper hydroxide on the surface of the glass pearls.

The fact that no surface relationship was found is the strongest indication that the adsorption is not physical. Whether the substance actually adsorbed is copper sulfate, copper ion or copper hydroxide, doubling the surface exposed should double the amount adsorbed, if the adsorption is physical. On the other hand, if the curve results from a chemical reaction occurring at the surface of the glass pearls, it is difficult to understand why increasing the concentration of copper sulfate decreases the amount of copper adsorbed.

The explanation given for the type of curve obtained is satisfactory for the results found experimentally. It requires that we assume that copper hydroxide is adsorbed. While this seems probable, and while it serves to explain the fact that a peculiar type of curve is obtained in this adsorption, the adsorption of copper hydroxide could not be shown experimentally.

### Summary.

1. This paper deals with the adsorption of copper from copper sulfate solution by glass and sand.
2. The concentration-adsorption curves show maximum values and do not correspond with the ordinary adsorption curves.
3. No relationship was found to exist between the total surface exposed and the amount adsorbed.

<sup>1</sup> Landolt-Börnstein Tabellen, p. 1190.



4. An explanation is given based on the assumption that adsorption of copper hydroxide, formed by hydrolysis, occurs. The adsorption belongs to the class of adsorptions known as "anomalous adsorptions."

5. The adsorption is considered to be physical in its nature, although the results do not definitely prove this point.

### PART III.—THE ADSORPTION OF IODINE BY STARCH.

**Introduction.**—In the two previous papers of this series adsorption values were obtained for the adsorption of a liquid by glass and for the adsorption of a solute by glass. In the first case several liquids were used as adsorbed substance and in the latter, water was used as the solvent and copper sulfate as the solute. In the present paper values are presented for the adsorption of a solute from an organic solvent. Values are also given for the adsorption of the vapor of the organic solvent, the vapor of the solute and the vapor of the solution.

Curves for pure vapor adsorptions are fairly numerous, as are those for solutes in water solution. For the most part they are of the type of ordinary adsorption curves. Some work has also been done on adsorption from organic solvents, notable that by Freundlich.<sup>1</sup> The effect of a solute which is volatile on the adsorption of the vapors of the solvent has not been determined. It may be considered as the adsorption of mixed vapors, and may be expected to give values which are specific for the substances used and also in a measure dependent on the vapor pressure of the solvent.

#### Materials.

**Adsorbed Substance.**—Iodine seemed best fitted for the purpose of this investigation. In the solid state its vapor pressure is slight but greater than that of most solids. Solutions could readily be made of it in almost any organic liquid, and it could be determined easily and accurately. In addition it was known to be strongly adsorbed by starch, the solid finally chosen in this piece of work, for adsorption purposes.

**Solvents.**—Three organic liquids were chosen as solvents for the iodine, these being alcohol, acetic acid and nitrobenzene. Alcohol has a relatively high vapor pressure, that of acetic acid is considerably smaller, and nitrobenzene has a vapor pressure of less than 1 mm. at ordinary temperatures. It was hoped that results with these three liquids would serve to determine whether the vapor pressure of the solvent played any part in determining the amount of the adsorbed vapor.

<sup>1</sup> *Z. Phys. Chem.*, 57, 385 (1906).

A tenth normal solution of iodine in each of these solvents was prepared, the resublimed iodine being weighed into a glass stoppered weighing bottle and the stoppered bottle being dropped into a measured volume of the solvent. After the iodine had dissolved the solution was transferred to a flask and additional solvent added to make the solution tenth normal. The actual amount of iodine present was checked by titrating a known volume of the solution with standardized solution of sodium thiosulfate.

**Adsorbing Substance.**—It was originally intended to use the glass pearls described in the previous papers as the adsorbing solid, in order to carry out the work with known surfaces. In an attempt to determine the amount of adsorption that might be expected, a preliminary set of determinations was run using a 30-gram sample of precipitated silica. The results obtained were positive in every case, indicating an adsorption, but were very small in amount. Since even smaller results might be expected with the glass pearls, it was decided that some other adsorbing medium was required, and that the surface factor could only be roughly controlled.

Starch was, therefore, substituted for the pearls. The starch made use of was coarsely ground so that it would pass a twenty-mesh sieve but would be held on one of forty mesh. It was dried at  $110^{\circ}$  for three hours previous to use.

### Method.

**1. Adsorption of Vapors of Pure Solvent and Pure Solute.**—Fifty cubic centimeters of one of the organic liquids was placed in the bottom of a five-inch desiccator having a tight fitting cover. Supported above the liquid was a glass stoppered weighing flask (open) containing a gram of the starch. At intervals the glass stoppered flask was capped, wiped dry, removed from the desiccator, let stand for an hour in the balance case and weighed. It was then replaced and the weighing continued. Weighings were made in the same way using each of the pure organic liquids and also pure iodine.

**2. Adsorption from Solution.**—Five grams of the starch described above was transferred to a 200-cc. flask. One hundred cc. of a tenth-normal solution of iodine was poured over it. The flask was closed with a ground glass stopper and well shaken. At the time intervals noted in the tables, 10-cc. portions were pipetted off with a carefully calibrated pipette and the iodine present determined. This series was run with each of the iodine solutions.

**3. Adsorption from Vapors of Tenth-Normal Solutions.**—The same apparatus and the same procedure was used for this series of determinations was used for the adsorptions of the vapors of the pure solvents. One gram of starch was used for each determination.



The work was all done without the use of a thermostat. Temperature readings taken at intervals did not indicate a temperature variation of more than two degrees.

TABLE I.

Vapors Adsorbed by 1 G. Starch from Pure Solvent and Pure Solute.

Time in hrs.	Nitrobenzene.	Time in hrs.	Alcohol.	Acetic acid.	Iodine.
23	0.0001	16	0.0290	0.0976	0.0379
47	0.0016	64	0.0295	0.1025	0.0448
71	0.0018	88	0.0300	0.1040	0.0448
96	0.0038	112	0.0313	....	0.0447
120	0.0058	136	0.0311	0.1081	0.0448
192	0.0108	...	....	....	....
240	0.0140	...	....	....	....

TABLE II.

Vapors Adsorbed by 1 G. Starch from  $N/10$  Solutions.

2	0.0073	0.0079	0.0182
6	0.0085	....	0.0220
24	0.0172	0.0228	0.0596
48	0.0235	0.0485	0.1019
72	0.0309	0.0671	0.1305
96	0.0421	....	0.1492
240	0.1064	0.0906	0.1969

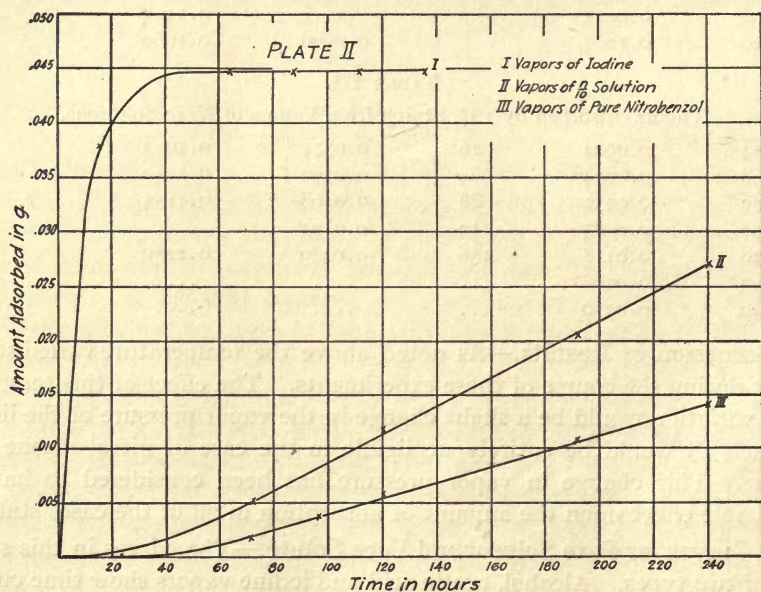
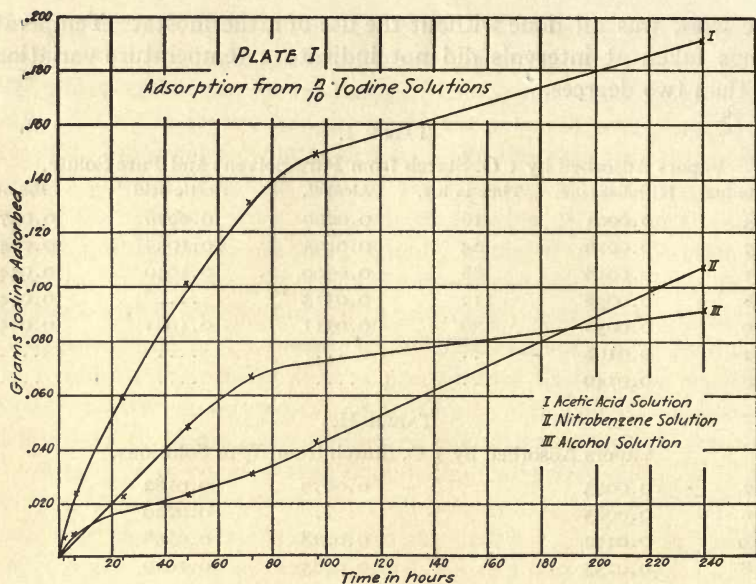
TABLE III.

Vapors Adsorbed by 1 G. Starch from Vapors of  $N/10$  Solutions.

24	0.0004	16	0.0371	0.1073
48	0.0034	64	0.0392	0.1140
72	0.0052	88	0.0406	0.1155
96	0.0085	112	0.0425	....
120	0.0118	136	0.0440	0.1250
192	0.0206	...	....	....
240	0.0270	...	....	....

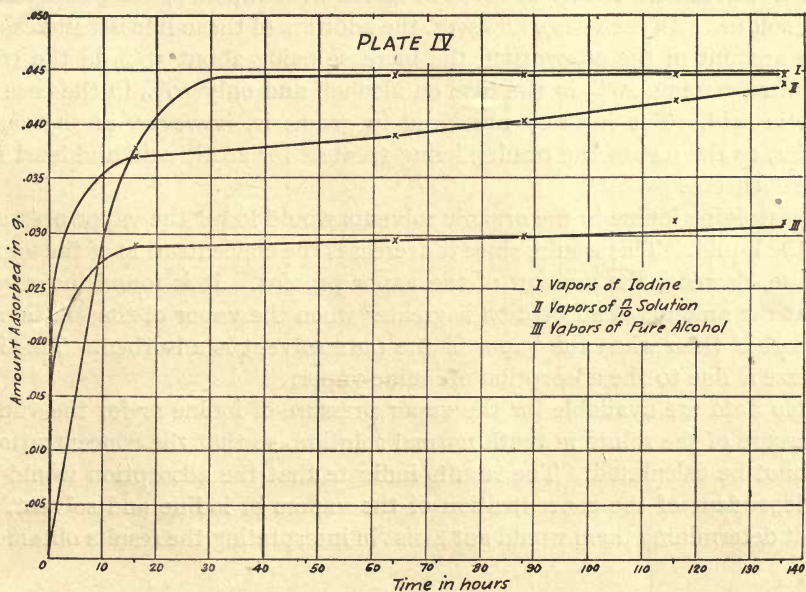
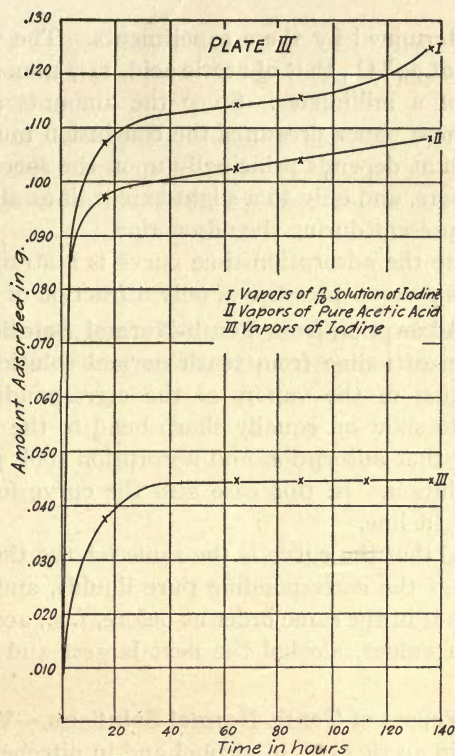
**Discussion of Results.**—As noted above the temperature varied somewhat during the course of these experiments. The effect of this temperature variation would be a slight change in the vapor pressure of the liquid in use. It would be entirely negligible in the case of nitrobenzene and iodine. This change in vapor pressure has been considered to have a negligible effect upon the amount of adsorption in all of the cases studied.

**1. Curves for Pure Solvent and Pure Solute.**—The curves in this series are of two types. Alcohol, acetic acid and iodine vapors show time curves that are typical for adsorptions. They rise within a relatively short time to about the maximum value and the adsorption increases gradually with time beyond that point over the whole period of the experiment. Alcohol vapor shows the least adsorption, iodine vapor the mean, and acetic acid vapor the maximum adsorption.



One of the objects of this series of experiments was to determine whether vapor pressure was an important factor in determining the adsorbed amount or whether the adsorption was specific for the liquid used, and only dependent on vapor pressure insofar as it supplies vapor for adsorption.





This has been determined by these experiments. The vapor pressure of alcohol is 44 mm. at  $20^{\circ}\text{C}$ ., that of acetic acid, 11.7 mm. and that of iodine only a fraction of a millimeter. Since the amounts adsorbed are not proportional to these vapor pressures the conclusion must be drawn that the adsorbed amount depends principally upon the specific affinity of the starch for the vapors, and only to a slight extent, if at all, upon the actual amount of vapor present during the adsorption.

For nitrobenzene the adsorption-time curve is a straight line. In this case the liquid has a vapor pressure of only a fraction of a millimeter.

**2. Curves for Adsorption from Tenth-Normal Solutions.**—The curves for the adsorption of iodine from tenth normal solutions are similar to those for adsorption of the vapors of the corresponding pure solvent, though they fail to show an equally sharp bend to the horizontal. This is due to the fact that adsorption and absorption took place at the same time from the solution. In this case also the curve for nitrobenzene is practically a straight line.

It may be noted that the curve is the same for the three solutions as it is for the vapors of the corresponding pure liquids, and that the magnitude of the results is in the same order as before, *i. e.*, acetic acid gives the largest adsorption values, alcohol the next largest and nitrobenzene the smallest values.

**3. Curves for Vapors of Tenth-Normal Solutions.**—Vapors from tenth-normal solutions in acetic acid, in alcohol and in nitrobenzene give curves which correspond closely to those obtained with vapors of the corresponding solutes. In each case, however, the addition of the iodine has increased the amount of the adsorption, the increase being about 50% in the case of nitrobenzene, 26% in the case on alcohol, and only 10% in the case of acetic acid. The increase measured in grams is, however, in the same order, as the rest of the results, being greatest for acetic acid and least for nitrobenzene.

Dissolving iodine in the organic solvents would lower the vapor pressure of the liquid. This would, since it decreases the concentration of the vapor phase, decrease the amount of the vapor present. It is found, however, that the amount of adsorption is greater when the vapor of the solution is adsorbed than when the vapor of the pure solvent is adsorbed. This increase is due to the adsorption of iodine vapor.

No data are available for the vapor pressure of iodine or for the vapor pressure of the solute in tenth normal solution, so that the concentrations cannot be calculated. The results indicate that the adsorption would be independent of the concentration of the vapors of iodine and solvent, so that determining them would not assist in interpreting the results obtained.



The starch assumed a light blue color when standing over the solution which proves that iodine was adsorbed. Its amount, however, was not determined.

The adsorption of the vapors of organic solvents and of iodine depend upon the specific affinity of starch for these substances and is not dependent on any physical properties common to the adsorbed substances.

This investigation was undertaken at the suggestion of Dr. I. H. Derby. I take this opportunity of expressing my sincerest thanks for his guidance and advice.













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